Photochemistry of Benzene Isomers. 2. Benzvalene and Dewar Benzene

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The photochemistry of two valences isomers of benzene, benzvalene and Dewar benzene, is such that they isomerize cleanly to yield benzene in high quantum yield.

Introduction

The valence isomers of benzene have held a fascination for chemists, theoreticians, and spectroscopists since the nineteenth century when Kekulé first published a structure for benzene which succeeded in explaining the chemical behavior of the molecule.

Several resonance forms of the benzene structure were proposed shortly thereafter, the structures of which are shown in the previous paper (part 1). Of course we now know that these structures are not canonical structures of planar benzene, but rather are bent molecules in their own right. As was explained in part 1 at least two or possibly three of the valence isomers are low yield photoproducts of benzene and may in turn be involved in a reversible photoisomerization process back to benzene, thus perhaps explaining the mysterious channel 3 energy dissipation process. Alternatively, the valence isomers can be thought of as local minima in the 31-dimensional potential surface of excited benzene that can trap the excitation and effectively provide a fast relaxation channel. The two valence isomers most often reported in benzene photochemistry are benzvalene and Dewar benzene. We report here the photochemical behavior of these isomers.



Experimental Section

Unsubstituted Dewar benzene was first synthesized by Van Temelen and Pappas.¹ We followed their synthetic method with minor modifications that are detailed elsewhere.²

Benzvalene can be synthesized in a one-step process from lithium cyclopentandienide and methylene chloride after Katz, Wang, and Acton.³

Purification and Handling. Dewar benzene was obtained from its synthesis in a tetradecane solution from which it was distilled on a vacuum line for a period of 24 h and trapped at 77 K into a sample vial containing 0.5 mL of redistilled *n*-heptane. Preparative gas chromatography of this solution on a 20% Squalane column at ambient temperature gave pure Dewar benzene which was stored under vacuum at 77 K.

Benzvalene was obtained from its synthesis in impure ether solution. For purification, an end fraction of this solution was chromatographed on a glass column packed with 8% didecylphthalate and 3% triethanolamine again at room temperature. Almost inevitably trace amounts of fulvene were present in the benzvalene. These could be

removed by trap-to-trap distillation from 195 to 77 K as fulvene has a significantly higher vapor pressure than benzvalene at 195 K. Purified benzvalene was also stored under grease-free vacuum conditions at 77 K.

Both valence isomers decompose violently in condensed form at 298 K and considerable care must be exercised during their handling and transfer. Techniques similar to those reported in part 1 were utilized. In the vapor phase, however, the isomers are stable, though benzvalene isomerizes to fulvene in a reaction that seems to be catalyzed by temperature and metal surfaces.

Photochemical techniques and product yield analysis have been described in the preceding paper.

Photochemistry of Benzvalene. Kaplan and Wilzbach⁴ first reported the photolysis of benzvalene at 254 nm in the presence of 101 kPa of nitrogen and found a 3:1 mixture of benzene and fulvene was formed with a quantum yield of 0.4. Subsequently, Renner et al.⁵ showed that photolysis of benzvalene in hydrocarbon solution at 254 nm produced benzene in low yield.

The absorption spectrum of benzvalene has been studied in some detail.⁶ Absorption begins smoothly around 280 nm, but the band develops strong, apparently vibronic, structure at 226 nm. This structure is not sharp, however, and the narrowest line has a half-width of 60 cm^{-1} . The band peaks at 217 nm ($\epsilon_{max} = 260 \text{ m}^2 \text{ mol}^{-1}$) and then decreases to 190 nm. Another absorption band has been reported in the vacuum ultraviolet that has a maximum at 178 nm. It has been suggested the structural part of the 217-nm absorption band is due to a Rydberg transition and the underlying continuum is assigned to a $\pi\pi^*$ (¹B₂ $^{1}A_{1}$) transition.⁷

In preliminary experiments we excited 13 Pa of pure benzvalene at 280, 265, and 254 nm. At first two excitation wavelengths very little photochemical decomposition was observed via monitoring the benzvalene absorption spectrum. The absorbance decreased by up to 5% but this disappearance of benzvalene may have been due to formation of fulvene by collision with the cell walls rather than any photochemistry as similar results were noticed by using nonconditioned cells without exposure to radiation. The extinction coefficient of benzvalene at these two wavelengths is very low ($<0.01 \text{ m}^2 \text{ mol}^{-1}$) so the results are not surprising. Photolysis at 254 nm where the extinction coefficient is about 1 m² mol⁻¹ was much more dramatic

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Figure 1. Photochemistry of benzvalene at 254 nm (a) before and (b) after 1-h exposure.

TABLE I: Wavelength Dependence of the QuantumYield of Benzene Production from $Benzvalene^{a}$

quantum yield ^b	std dev	
0.715	0.100	
0.678	0.076	
0.603	0.033	
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^a Sample pressure was 13 Pa (0.1 torr) and photolysis was for 1 h. ^b Mean of five determinations.

and the change in the benzvalene absorption spectrum after irradiating a 13 Pa sample for 1 h is shown in Figure 1. The product that forms at this wavelength is clearly benzene from its characteristic absorption from 260 to 240 nm. The photochemical behavior is very clean and no products other than benzene appear to form.

The results of the determination of the quantum yield of benzene formation from benzvalene for 254, 240 and 225 nm are shown in Table I. These yields were determined by using the same procedures used for fulvene photochemistry in the preceding paper.

One difficulty in the benzvalene photochemical experiments is the facile isomerization of benzvalene to fulvene. We do not believe this is a photochemical reaction although a two-step reaction benzvalene \rightarrow fulvene \rightarrow benzene cannot be absolutely eliminated as a possible mechanism. When chromatographing the irradiated benzvalene only two peaks aside from the solvent were eluted and these were identified as fulvene and benzene. Analysis of an unirradiated sample of benzvalene yielded only fulvene so that benzvalene obviously converts to fulvene on the column. No trace of benzene was found in the unirradiated benzvalene hence the benzene found in photolyzed samples was solely the result of photochemical isomerization.

It can be seen from Table I that the quantum yield of benzene formation from benzvalene excited at wavelengths shorter than 260 nm is high and appears to decrease with decreasing excitation wavelength. This effect is probably due to two factors. First, as mentioned, the absorption spectrum has been assigned as due to two overlapping transitions, one primarily to a valence state and the other to a state that is principally Rydberg in nature. Absorption of light intensity by the Rydberg state may lower the measured quantum yield of benzene formation that occurs from the valence state. Second, there is the possibility of the formation of fulvene by photochemistry of benzvalene. If such a photochemical rearrangement does occur, then



Figure 2. Photochemistry of Dewar benzene at 240 nm (a) before and (b) after 1-h exposure. The spectra have been offset for clarity.

TABLE II:	Wavelength Dependence of the Quantum	
Yield of Ben	zene Production from Dewar Benzene ^a	

λ, nm	quantum yield ^b	std dev
265	0.907	0.142
254	0.983	0.062
245	0.982	0.044
225	0.921	0.107

^a Sample pressure was 13 Pa (0.1 torr) and photolysis was for 1 h. ^b Mean of five determinations.

the fulvene so formed would itself isomerize to benzene and the observed decrease in quantum yield of benzene formation would parallel the trend observed for fulvene shown in part 1.

Photochemistry of Dewar Benzene. The vapor-phase absorption spectrum of Dewar benzene begins around 265 nm and rises gradually without any sign of structure to a maximum at 205 nm.⁸ A second band, which initially shows well-developed structure built onto continuously rising absorption, begins at 203 nm. By 185 nm this band also becomes structureless and absorption continues below 185 nm with no observable maximum. Both systems are weak and the measured oscillator strengths are 0.023 and 0.04 for the first and second bands, respectively. On the basis of this, the first band is assigned as a forbidden $\pi\pi^*$ (¹A₂-¹A₁) transition. The second band has again been shown to have predominate Rydberg character.⁷

Figure 2 shows the results of irradiation of Dewar benzene at 240 nm after a 1-h exposure. Clearly, benzene is produced as the Dewar benzene is photolyzed. The isobestic point at 206 nm is indicative of the formation of only one species that absorbs in the wavelength region scanned. The rate of benzene formation was low at this wavelength, but as the fraction of light absorbed is also quite low, the quantum efficiency may be quite high. Polymer formation was negligible even over a 4-h photolysis and no benzene formation was detected in unirradiated samples over periods in excess of 5 h.

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Photochemistry of Benzvalene and Dewar Benzene



Figure 3. Relative energies of the known electronic states of some benzene isomers.

Quantum yield measurements confirmed that benzene forms efficiently from Dewar benzene. The yields at various wavelengths are shown in Table II. The chromatographic techniques also confirmed that no other products are formed other than benzene. In contrast to benzvalene, there does not appear to be any wavelength dependence of the quantum yield. Because of the low fraction of light absorbed, the errors in the quantum yield determinations are rather large. Nevertheless, the quantum yields of benzene formation are unquestionably high and may, in fact, be unity.

Discussion

A picture is beginning to emerge for the interrelationships of the various isomers in their electronic states. Since the ground states of the valence isomers are totally symmetric they all lie on the same zero-order potential surface. If the state correlation methods of Longuet-Higgins and Abrahamson are used,⁹ the ¹B₂ benzvalene state correlates directly with the ¹B_{1u} state of benzene. Similarly, the ¹A₂ state of Dewar benzene correlates with a benzene ¹E_{2g} state. Very fast interconversion between these directly coupled states readily accounts for the photochemical behavior of the benzene isomers. However, when considering the photochemistry of benzene itself, we must consider both symmetry allowedness and the energetic feasibility of any interconversion. Relative ground-state energies of the

(9) Longuet-Higgins, H. C.; Abrahamson, E. W. J. Am. Chem. Soc. 1965, 87, 2045-6.

unsubstituted isomers have not been determined experimentally, but calculations using the MINDO technique¹⁰ parameterized to yield reliable heats of formation are shown in Figure 3. If these values are at all accurate, they illustrate clearly that absolute energy considerations may be more important than symmetry arguments. For example, Bryce-Smith et al.¹¹ have shown that Dewar benzene forms from the S_2 (¹ B_{1u}) state of benzene, but not from S_1 $({}^{1}B_{2u})$ and suggest the reason to be that a symmetry-allowed pathway exists from ${}^{1}B_{1u}$ whereas there is none from ${}^{1}B_{2u}$. However, it is clear from Figure 3 that excitation (48500 cm^{-1}) into S₂ which produced the isomerization is about 7000 cm⁻¹ short of even the lowest Dewar benzene excited singlet state. It thus seems likely that the electronic symmetry-allowed process is energetically inaccessible. We know nothing of the available Dewar benzene triplet states, however, except that the lowest should be lower than the ${}^{1}A_{2}$ state. Triplet states of Dewar benzene may then be energetically accessible to ${}^{1}B_{1u}$ benzene, but it has been shown¹¹ that triplet benzene is not involved in the isomerization to Dewar benzene. We consider the conversion of singlet benzene to triplet Dewar benzene, although perhaps energetically feasible, to be a less likely alternative to a spin-allowed process, since the spectral diffuseness in the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ benzene transition indicates a nonradiative decay rate of ${}^{1}B_{1u}$ of at least $10^{13} s^{-1}$. This seems very fast for a spin-forbidden process. We conclude that the isomerization then probably occurs in an orbitally forbidden, but spin-allowed process such as by a vibronic mechanism.

Similar energetic considerations apply to any photochemistry from ${}^{1}B_{2u}$ benzene. Again from Figure 3 it is apparent that the only valence isomer singlet states energetically accessible to ${}^{1}B_{2u}$ benzene are the ground states. Triplet states may be accessible, but the channel 3 relaxation seems too fast $(>10^{11} \text{ s}^{-1})$ for a spin-forbidden process. Transitions from ${}^{1}B_{2u}$ benzene to all the isomer ground states are symmetry forbidden, so vibronic or other mechanisms are implied. If in fact the channel 3 relaxation of benzene is at least in part due to photochemistry involving the valence isomers, the two possible mechanisms, i.e., a reversible photoisomerization or local minima in the benzene ¹B_{2u} potential surface representing the isomer ground states, cannot be distinguished at this stage. However, there is no doubt that there are extensive photochemical interrelationships between benzene and its valence isomers. Further work, albeit experimentally difficult, using time-resolved single vibronic level photochemistry could provide the answers.

Acknowledgment. This work was supported by the Australian Research Grants Committee.

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